Generalized von Smoluchowski model of reaction rates, with reacting particles and a mobile trap

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We study diffusion-limited coalescence, $A + A \rightleftharpoons A$, in one dimension, in the presence of a *diffusing* trap. The system may be regarded as a generalization of von Smoluchowski's model for reaction rates, in that: (a) it includes reactions between the particles surrounding the trap, and (b) the trap is mobile—both considerations which render the model more physically relevant. As seen from the trap's frame of reference, the motion of the particles is highly correlated, because of the motion of the trap. An exact description of the long-time asymptotic limit is found using the IPDF method, and exploiting a "shielding" property of reversible coalescence that was discovered recently. In the case where the trap also acts as a source—giving birth to particles—the shielding property breaks down, but we find an "equivalence principle": Trapping and diffusion of the trap may be compensated by an appropriate rate of birth, such that the steady state of the system is identical with the equilibrium state in the absence of a trap.

I. INTRODUCTION

Non-equilibrium kinetics of diffusion-limited reactions has been the subject of much recent interest [1–6]. While equilibrium systems can be completely analyzed by means of standard thermodynamics methods, and reaction-limited processes are well described by classical rate equations [7,8], there exist no such general approaches to the problem of non-equilibrium, diffusion-limited reactions.

A fundamental model for the reaction rate in diffusion-limited processes had been presented by von Smoluchowski [9]. In this model, an ideal spherical trap is surrounded by a swarm of Brownian particles. The rate of absorption of particles into the spherical trap models the reaction rate. The Smoluchowski model is limited in two important respects: (a) the particles react with the spherical trap but *not* with each other, and (b) the trap itself does not diffuse, but remains static at the origin. Both limitations are unphysical: In real reaction processes all particles interact (and may react) with each other, and *all* particles are mobile.

Several attempts have been made to remove the restriction of an immobile trap [10–12]. The problem is complicated by the apparent correlations in the motion of the surrounding particles: With a mobile trap, the motion of the surrounding particles is highly correlated, since a step of the trap to the left, say, in the lab frame of reference, results in an apparent step to the right of *all* the surrounding particles in unison, in the trap's frame of reference. Results are restricted to empirical formulas inspired by numerical simulations [10], or to a number of special cases (immobile particles [11]; short times [12]). As regards reactions between the surrounding particles, these could hardly be considered, other than numerically, because few models of diffusion-limited kinetics yield themselves to exact analysis. In fact, diffusion-limited coalescence ($A + A \rightarrow A$) and annihilation ($A + A \rightarrow 0$) in one dimension alone account for most of the known exact results [13–23].

Recently, we have studied reversible coalescence, $A + A \rightleftharpoons A$, on the line and in the presence of a *static* trap [24]. An exact analysis is possible with the method of interparticle distribution functions (IPDF) [25]. We have found a remarkable property of "shielding": The particle nearest to the trap effectively shields the remaining particles from the trap. The steady state of the system is uniquely characterized by the distance of the nearest particle to the trap—all other particles remain distributed exactly as in the equilibrium state of the system in the absence of a trap. This shielding property persists even in the presence of a bias field (convection, or drift).

In this paper we consider reversible coalescence with a *mobile* trap which diffuses with a diffusion constant D_T, not necessarily equal to the diffusion constant of the surrounding particles, D. The problem may still be formulated with the IPDF method, in spite of the correlations induced by the motion of the trap. The shielding property of the nearest particle to the trap also remains in effect, and it enables us to find a complete exact description of the

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distribution of particles in the long-time asymptotic limit. We find that relative to the trap the surrounding particles remain at equilibrium, but the gap to the nearest particle is proportional to $D + D_T$.

An interesting generalization is to the case when the backward process $A \to A + A$ is not limited to the particles alone, but the trap too may act as a source. Again, the rate of generation of particles from the trap, v_T, need not coincide with v, the production rate from the reverse birth reaction. We find that if $v_T > 0$ the shielding property breaks down, and we are unable to derive a complete exact description of the system. However, if the birth rate is $v_T = v(1 + D_T/D)$, the effect of the trap is nullified: The particles remain distributed as in equilibrium, as if the trap were not present.

The remainder of this paper is organized as follows. In section II we review the coalescence process and the IPDF method used for its analysis. The model with a mobile trap is considered in section III. In section IV, we generalize to the case where the trap may also act as a source. We conclude with a summary and discussion, in section V.

II. COALESCENCE AND THE IPDF METHOD

Our model [13,14,25] is defined on a one-dimensional lattice of lattice spacing a. Each site is in one of two states: occupied by a particle A ($\bullet$), or empty ($\circ$). Particles hop randomly to the nearest neighbor site to their right or left, at rate D/a^2. Thus, in the continuum limit of $a \to 0$ the particles undergo diffusion with a diffusion constant D. A particle may give birth to an additional particle, into a nearest neighbor site, at rate v/a (on either side of the particle)[1]. If hopping or birth occurs into a site which is already occupied, the target site remains occupied. The last rule means that coalescence, $A + A \to A$, takes place *immediately* upon encounter of any two particles. Thus, the system models the diffusion-limited reaction process

$$A + A \rightleftharpoons A . \tag{1}$$

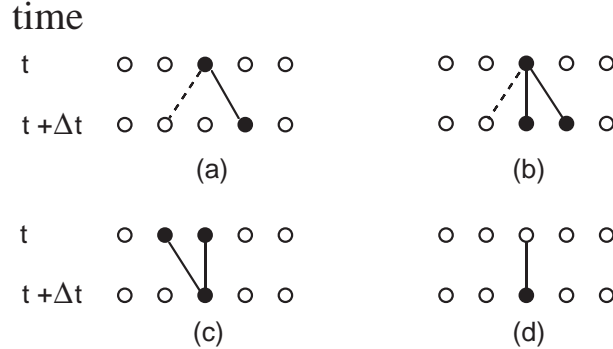The dynamical rules of the model are illustrated in Fig. 1.

Figure 1 Reaction rules: (a) diffusion; (b) birth; and coalescence, (c) following diffusion, and (d) following a birth event. The broken lines in (a) and (b) indicate alternative target sites.

An exact treatment of the problem is possible through the method of Empty Intervals, known also as the method of Inter-Particle Distribution Functions (IPDF) [25]. The key concept is $E_{n,m}(t)$—the probability that sites $n, n + 1, \cdots, m$ are empty at time t. The probability that site n is occupied is

$$\text{Prob}(\text{site } n \text{ is occupied}) \equiv \text{Prob}(\overset{n}{\bullet}) = 1 - E_{n,n} . \tag{2}$$

The event that sites n through m are empty (prob. $E_{n,m}$) consists of two cases: site $m + 1$ is also empty (prob. $E_{n,m+1}$), or it is occupied. Thus, the probability that sites n through m are empty but site $m + 1$ is occupied, is

$$\text{Prob}(\overset{n}{\circ} \cdots \overset{m}{\circ} \bullet) = E_{n,m} - E_{n,m+1} , \tag{3}$$

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[1]Our notation here differs from previous work: we take the birth rate to be v/a rather than $v/2a$, to achieve a more aesthetic form of the final result.

and likewise,

$$\text{Prob}(\bullet \overset{n}{\circ} \cdots \overset{m}{\circ}) = E_{n,m} - E_{n-1,m} \ . \tag{4}$$

With this in mind, one can write down a rate equation for the evolution of the empty interval probabilities:

$$\begin{aligned}
\frac{\partial E_{n,m}}{\partial t} &= \frac{D}{a^2}(E_{n,m-1} - E_{n,m}) \\
&- \frac{D}{a^2}(E_{n,m} - E_{n,m+1}) \\
&+ \frac{D}{a^2}(E_{n+1,m} - E_{n,m}) \\
&- \frac{D}{a^2}(E_{n,m} - E_{n-1,m}) \\
&- \frac{v}{a}[(E_{n,m} - E_{n,m+1}) + (E_{n,m} - E_{n-1,m})] \ .
\end{aligned} \tag{5}$$

For example, the first term on the r.h.s. of Eq. (5) accounts for the increase in $E_{n,m}$ when the particle at the right edge of $\overset{n}{\circ} \cdots \circ \overset{m}{\bullet}$ hops to the right and the sites $n, \ldots, m$ become empty; the second term denotes the decrease in $E_{n,m}$ when a particle at $m+1$ hops to the left into the empty interval $n, \ldots, m$, and so on.

Eq. (5) is valid for $m > n$. The special case of $m = n$ corresponds to $E_{n,n}$—the probability that site n is empty. It is described by the equation

$$\begin{aligned}
\frac{\partial E_{n,n}}{\partial t} &= \frac{D}{a^2}(1 - E_{n,n}) \\
&- \frac{D}{a^2}(E_{n,n} - E_{n,n+1}) \\
&+ \frac{D}{a^2}(1 - E_{n,n}) \\
&- \frac{D}{a^2}(E_{n,n} - E_{n-1,n}) \\
&- \frac{v}{a}[(E_{n,n} - E_{n,n+1}) + (E_{n,n} - E_{n-1,n})] \ .
\end{aligned} \tag{6}$$

Comparison with Eq. (5) yields the boundary condition: $E_{n,n-1} = 1$. The fact that the $\{E_{n,m}\}$ represent *probabilities* implies the additional condition that $E_{n,m} \geq 0$. Finally, if the system is not empty then $\lim_{\substack{n \to -\infty \\ m \to +\infty}} E_{n,m} = 0$.

In many applications, it is simpler to pass to the continuum limit. We write $x = na$ and $y = ma$, and replace $E_{n,m}(t)$ with $E(x,y,t)$. Letting $a \to 0$, Eq. (5) becomes

$$\frac{\partial}{\partial t} E = D \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right) E - v \left(\frac{\partial}{\partial x} - \frac{\partial}{\partial y} \right) E \ , \tag{7}$$

with the boundary conditions,

$$E(x,x,t) = 1 \ , \tag{8}$$
$$E(x,y,t) \geq 0 \ , \tag{9}$$
$$\lim_{\substack{x \to -\infty \\ y \to +\infty}} E(x,y,t) = 0 \ . \tag{10}$$

The concentration becomes

$$\rho(x,t) = -\frac{\partial}{\partial y} E(x,y,t)|_{y=x} \ , \tag{11}$$

and one can also show that the conditional joint probability for having particles at x and y but none in between, is

$$P_2(x,y,t) = -\frac{\partial^2}{\partial x \, \partial y} E(x,y,t) \ . \tag{12}$$

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From P_2 one obtains the "forward" (and also "backward") IPDF—the probability that given a particle at x (y) the next nearest particle to its right (left) is at y (x):

$$p_f(x, y, t) = \rho(x, t)^{-1} P_2(x, y, t) ; \qquad p_b(x, y, t) = \rho(y, t)^{-1} P_2(x, y, t) . \tag{13}$$

The IPDF method can also handle multiple-point correlation functions [14]. Let $E_n(x_1, y_1, x_2, y_2, \ldots, x_n, y_n, t)$ be the joint probability that the intervals $[x_i, y_i]$ ($i = 1, 2, \ldots, n$) are empty at time t. The intervals are non-overlapping, and ordered: $x_1 < y_1 < \cdots < x_n < y_n$. Then, the n-point correlation function (the probability of finding particles at $x_1, x_2, \ldots, x_n$ at time t) is given by

$$\rho_n(x_1, \ldots, x_n, t) = (-1)^n \frac{\partial^n}{\partial y_1 \cdots \partial y_n} E_n(x_1, y_1, \ldots, x_n, y_n, t)|_{y_1 = x_1, \ldots, y_n = x_n} . \tag{14}$$

For reversible coalescence, the E_n satisfy the partial differential equation:

$$\begin{aligned}
\frac{\partial}{\partial t} E_n(x_1, y_1, \ldots, x_n, y_n, t) =& D \left(\frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial y_1^2} + \cdots + \frac{\partial^2}{\partial x_n^2} + \frac{\partial^2}{\partial y_n^2} \right) E_n \\
&- v \left[\left(\frac{\partial}{\partial x_1} - \frac{\partial}{\partial y_1} \right) + \cdots + \left(\frac{\partial}{\partial x_n} - \frac{\partial}{\partial y_n} \right) \right] E_n ,
\end{aligned} \tag{15}$$

with the boundary conditions

$$\lim_{x_i \uparrow y_i \text{ or } y_i \downarrow x_i} E_n(x_1, y_1, \ldots, x_n, y_n, t) = E_{n-1}(x_1, y_1, \ldots, \cancel{x_i}, \cancel{y_i}, \ldots, x_n, y_n, t) , \tag{16}$$

and

$$\lim_{y_i \uparrow x_{i+1} \text{ or } x_{i+1} \downarrow y_i} E_n(x_1, y_1, \ldots, x_n, y_n, t) = E_{n-1}(x_1, y_1, \ldots, \cancel{y_i}, \cancel{x_{i+1}}, \ldots, x_n, y_n, t) . \tag{17}$$

For convenience, we use the notation that crossed out arguments (e.g. $\cancel{x_i}$) have been removed. The E_n are tied together in an hierarchical fashion through the boundary conditions (16) and (17): one must know E_{n-1} in order to compute E_n.

As a trivial example, consider the homogeneous steady state of reversible coalescence. This is in fact an *equilibrium* state, which satisfies detailed balance. The particles are simply distributed completely randomly—a state which maximizes their entropy. One obtains

$$E_{n,\text{eq}} = \exp\{-\gamma[(y_1 - x_1) + \cdots + (y_n - x_n)]\} , \tag{18}$$

and

$$\rho_{n,\text{eq}}(x_1, x_2, \ldots, x_n) = \gamma^n , \tag{19}$$

where $\gamma \equiv v/D$ is the particle concentration at equilibrium.

III. COALESCENCE WITH A MOBILE TRAP

We now consider the coalescence model but with a trap which diffuses with a diffusion constant D_T: In the discrete representation, the trap hops to its right or left at rate D_T/a^2. A particle that hops into the trap is irreversibly captured by it. Similarly, when the trap hops onto an occupied site it captures the particle in that site. It is convenient to analyze the system in the trap's frame of reference. In this view, the trap remains static at a site which we choose to be the origin; $n = 0$. When the trap does not move (in the lab frame of reference) the changes to $E_{n,m}$ are described by Eq. (5). A motion of the trap is perceived as a coherent opposite motion of the particles in the trap's reference frame. Thus, the changes to $E_{n,m}$ due to the motion of the trap are:

$$\begin{aligned}
\frac{\partial}{\partial t} (E_{n,m})_{\text{trap}} =& \frac{D_T}{a^2} [(E_{n+1,m+1} - E_{n,m+1}) + (E_{n-1,m-1} - E_{n-1,m}) \\
&- (E_{n,m} - E_{n-1,m}) - (E_{n,m} - E_{n,m+1})] .
\end{aligned} \tag{20}$$

For example, the first term on the r.h.s. denotes the possibility that site $n + 1$ is occupied while the subsequent sites $n + 2, n + 3, \ldots, m + 1$ are empty, and the trap hops to the right: In the trap's frame of reference the particle at $n + 1$

seems to hop to the left, thereby clearing the $[n, m]$-interval. Notice that it is important to make sure that site $m+1$ is empty, since otherwise site m would become occupied as the trap moves to the right.

Putting together all the terms in (5) and (20), and passing to the continuum limit, we obtain

$$\frac{\partial}{\partial t}E = (D + D_{\mathrm{T}})(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2})E + 2D_{\mathrm{T}}\frac{\partial^2}{\partial x \partial y}E - v(\frac{\partial}{\partial x} - \frac{\partial}{\partial y})E \ , \tag{21}$$

which is now valid in the infinite wedge $0 < x < y$. The term with the mixed derivative is special: it arises because of the correlated motion of the particles in the reference frame of the trap.

The trap at $n = 0$ could be realized by holding that site empty, at all times. Thus, it follows that $E_{1,m} = E_{0,m}$, which results in the boundary condition (in the continuum limit):

$$\frac{\partial}{\partial x}E(x, y, t)|_{x=0} = 0 \ . \tag{22}$$

In addition, the boundary condition (10) becomes

$$\lim_{y \to \infty} E(x, y, t) = 0 \ , \tag{23}$$

while (8) and (9) still apply, without change.

We now search for a solution of Eq. (21), with the boundary conditions (8), (9), (22), and (23), in the long-time asymptotic limit, $\partial E/\partial t = 0$. It is simple to find eigenfunctions which obey Eq. (8), and other eigenfunctions which obey Eq. (22), but we were unable to devise a systematic method for finding the linear combinations that would satisfy both conditions simultaneously. Instead, we offer a solution based on the newly discovered property of "shielding" in the coalescence model [24,26].

In the steady state of the coalescence model with a *static* trap, it is found that the particles are distributed randomly, exactly as in the equilibrium state of the homogeneous, infinite system (end of section II). The system is then fully characterized by $p(z)$—the density distribution function of the distance between the trap and the nearest particle to the trap, z. The nearest particle effectively shields the remaining particles from the trap (Fig. 2). As we show below, the same shielding effect takes place even when the trap is mobile.
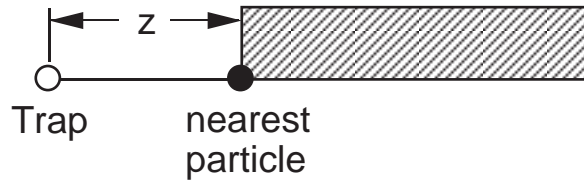

Figure 2. Schematic illustration of the shielding effect: The particles in the shaded area are distributed randomly and independently from each other, as in equilibrium. The gap z between the particles and the trap follows the probability density distribution $p_0(z)$.

Assuming that shielding holds, let $E(x, y|z)$ be the conditional probability that the interval $[x, y]$ is empty, given that the nearest particle to the trap is at z, then:

$$E(x, y|z) = \begin{cases} 1, & x < y < z \ , \\ 0, & x < z < y \ , \\ e^{-\gamma(y-x)}, & z < x < y \ . \end{cases} \tag{24}$$

Hence,

$$E(x, y) = \int_0^\infty E(x, y|z)p(z)\, dz = \int_y^\infty p(z)\, dz + e^{-\gamma(y-x)} \int_0^x p(z)\, dz$$

$$= 1 - F(y) + e^{-\gamma(y-x)}F(x) \ , \tag{25}$$

where in the last equation we introduced the definition

$$F(z) \equiv \int_0^z p(z')\, dz' \ . \tag{26}$$

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If the hypothesis of shielding is correct, the particle concentration can be obtained from Eqs. (11) and (25):

$$\rho(x) = p(x) + \gamma F(x) . \tag{27}$$

Substituting $E(x, y)$ from Eq. (25) into Eq. (21), in the stationary limit, the variables separate:

$$[(D + D_{\mathrm{T}})\frac{\partial^2}{\partial x^2}F(x) + v\frac{\partial}{\partial x}F(x)]e^{\gamma x} = [(D + D_{\mathrm{T}})\frac{\partial^2}{\partial y^2}F(y) + v\frac{\partial}{\partial y}F(y)]e^{\gamma y} , \tag{28}$$

and so, one is lead to the conclusion that

$$(D + D_{\mathrm{T}})\frac{d^2}{dz^2}F(z) + v\frac{d}{dz}F(z) = C'e^{-\gamma z} , \tag{29}$$

where C' is a constant.

The general solution of Eq. (29) is

$$F(z) = A + Be^{-\gamma'z} + Ce^{-\gamma z} , \tag{30}$$

where A, B, and $C = C'D^2/v^2 D_{\mathrm{T}}$ are constants, to be determined from boundary conditions. From the definition of F, we have; $F(0) = 0$, $\lim_{z\to\infty} F(z) = 1$, and $F(z) \geq 0$. The boundary condition due to the presence of the trap (Eq. 22) translates into $dF/dz|_{z=0} = 0$. Thus, we find

$$F(z) = 1 + \frac{D}{D_{\mathrm{T}}}e^{-\gamma z} - \frac{D + D_{\mathrm{T}}}{D_{\mathrm{T}}}e^{-\gamma'z} , \tag{31}$$

where $\gamma' \equiv v/(D + D_{\mathrm{T}})$. It then follows that

$$p(z) = \frac{v}{D_{\mathrm{T}}}(e^{-\gamma'z} - e^{-\gamma z}) . \tag{32}$$

From $p(z)$ one immediately obtains the average distance between the trap and the nearest particle: $(2D + D_{\mathrm{T}})/v$, as well as the particle concentration in the trap's frame of reference (Eq. 27):

$$\rho(x) = \gamma(1 - e^{-\gamma'x}) . \tag{33}$$

The last result is similar to the one obtained for a static trap, only that the width of the depletion zone near the trap is $1/\gamma' = (D + D_{\mathrm{T}})/v$, instead of $1/\gamma = D/v$.

Our original goal of finding the empty interval probability has now been achieved. Using (25) and (31), we get

$$E(x, y) = e^{-\gamma(y-x)} + \frac{D + D_{\mathrm{T}}}{D_{\mathrm{T}}}e^{-\gamma'y}[1 - e^{-(\gamma-\gamma')(y-x)}] . \tag{34}$$

This solution can be verified by direct substitution in Eq. (21) and in the boundary conditions (8), (22), and (23). The fact that we have found a solution proves that shielding indeed takes place, even with a mobile trap. On the other hand, we have merely shown that $E(x, y)$ is consistent with the shielding assumption. We now wish to show that the same is true for the whole hierarchy of E_n's, and hence for all n-point correlation functions.

If the particles are distributed as implied by shielding, then, following a reasoning similar to that which led to Eq. (25), we should have

$$\begin{aligned}
E_n(x_1, y_1, \ldots, x_n, y_n) &= 1 - F(y_n) \\
&+ e^{-\gamma(y_n - x_n)}[F(x_n) - F(y_{n-1})] \\
&+ \cdots + e^{-\gamma\{(y_n - x_n) + \cdots + (y_i - x_i)\}}[F(x_i) - F(y_{i-1})] \\
&+ \cdots + e^{-\gamma\{(y_n - x_n) + \cdots + (y_1 - x_1)\}}F(x_1) .
\end{aligned} \tag{35}$$

It is easy to confirm that these functions fulfill the boundary conditions (16) and (17). Eq. (15) is also satisfied, provided that F satisfies the same equation as above, Eq. (29), with the same boundary conditions. That is, the solution found above for F, combined with Eq. (35), solves the problem of the E_n. Indeed, using Eqs. (27), (14), and (35), we find the n-point correlation function:

$$\rho_n(x_1, \ldots, x_n) = \rho(x_1)\gamma^{n-1} , \tag{36}$$

exactly as we expect from a system with the shielding property.

IV. COALESCENCE WITH A TRAP-SOURCE

We now wish to consider a further generalization of the trapping problem. Suppose that the trap is imperfect, in the sense that it may also act as a source: the trap gives birth to A particles into the site next to it, at rate v_T/a. When $D_T = D$ and $v_T = v$ the trap is identical to the rest of the particles (only that the system is empty to the left of the trap). Thus, such a trap-source might also be viewed as a special, tagged particle, characterized perhaps by a different diffusing constant and back reaction rate. The model constitutes a modest first step towards the understanding of the more realistic situation where the size of aggregates matters, and clusters diffuse and give birth at different rates, determined by their accumulated mass. A very recent application is to the evolution of bacterial colonies living near a patch of nutrients. Nelson et al., [27,28] analyze such experiments with a diffusion-limited coalescence model with a source (modeling the nutrients) similar to ours.

The evolution equation for empty intervals in the trap-source model is identical to that of a perfect trap (Eq. 21). The birth of particles from the trap affects only the boundary condition at $x = 0$: it is no longer true that the trap may be realized by simply holding site $n = 0$ empty. To derive the appropriate boundary condition we consider the total changes to $E_{n,m}$, which are obtained by putting together Eqs. (5) and (20). The case of $n = 1$ needs to be considered separately, since we do not know what is $E_{0,m}$. The changes to $E_{1,m}$, including birth from the trap, add up to:

$$\frac{\partial}{\partial t} E_{1,m} = \frac{D}{a^2}[(E_{1,m-1} - E_{1,m}) - (E_{1,m} - E_{1,m+1}) + (E_{2,m} - E_{1,m})]$$
$$+ \frac{D_T}{a^2}[(E_{2,m+1} - E_{1,m+1}) - (E_{1,m} - E_{1,m+1}) + (E_{1,m-1} - E_{1,m})]$$
$$- \frac{v}{a}(E_{1,m} - E_{1,m+1}) - \frac{v_T}{a} E_{1,m} \ . \tag{37}$$

Comparison of this equation with that for general n, when $n = 1$, yields the discrete boundary condition:

$$(\frac{D}{a^2} + \frac{v}{a})(E_{1,m} - E_{0,m}) + \frac{D_T}{a^2}(E_{1,m-1} - E_{0,m-1}) = \frac{v_T}{a} E_{1,m} \ . \tag{38}$$

Notice that when $v_T = 0$ this reduces to $E_{0,m} = E_{1,m}$, as for a perfect trap. Passing to the continuum limit, the boundary condition for the trap-source becomes

$$(D + D_T)\frac{\partial}{\partial x} E(x, y, t)|_{x=0} = v_T E(0, y, t) \ . \tag{39}$$

We now seek a solution to Eq. (21), in the stationary limit $\partial E/\partial t = 0$, and which satisfies the boundary conditions (8), (9), (23), and (39). Assuming that shielding holds, we follow the same steps as in section III and we arrive at exactly the same result; $F(z) = A + Be^{-\gamma' z} + Ce^{-\gamma z}$, only that now the boundary condition $dF/dz|_{z=0} = 0$ is replaced by:

$$(D + D_T)e^{-\gamma z}\frac{d}{dz}F(z)|_{z=0} = v_T[1 - F(z)] \ , \tag{40}$$

from Eq. (39). (Again, notice that when $v_T = 0$ one recovers the condition $dF/dz|_{z=0} = 0$.)

From the boundary condition $F(\infty) = 1$, we obtain $A = 1$. Furthermore, from $F(0) = 0$ we get $B = -(1 + C)$. Finally, from the boundary condition due to the trap-source, Eq. (40), we get

$$[\frac{v_T}{v}\gamma' e^{(\gamma - \gamma')z} - 1](1 + C) = (\frac{v_T}{v}\gamma' - \gamma)C \ . \tag{41}$$

This condition cannot be satisfied for all z generically, and so one must conclude that *shielding does not take place in the system with a trap-source*. On the other hand, for the special case that $C = -1$ and $\gamma' v_T/v = \gamma$, Eq. (41) is satisfied. In this case $F(z) = 1 - e^{-\gamma z}$, which leads to $E = e^{-\gamma(y-x)}$ and $\rho(x) = \gamma$. That is, the particles are distributed exactly as in equilibrium, as if there were no trap! Thus, there exists a whole class of states which are equivalent to the equilibrium state of the infinite, homogeneous system, without a trap. The equivalent states are characterized by the relation

$$v_T = v(1 + \frac{D_T}{D}) \ . \tag{42}$$

For these states the effect of the trap is nullified. A larger diffusivity of the trap, D_T, (i.e., a larger trapping efficiency) is exactly compensated by an increasing rate of birth v_T from the trap-source.

An interesting case is when $D_T = D$ and $v_T = v$. Then the trap is identical to the surrounding particles. Notice, however, that this is *not* a "special" state (Eq. 42 is not satisfied), and hence we conclude that at the equilibrium state the system seems *inhomogeneous* from the point of view of a tagged particle. To shed some light on these baffling results, we first point out that since the equilibrium state is homogeneous it is perceived without change by any moving observer which does not interact with the particles, including random walkers. [Indeed, the equilibrium state $E = e^{-\gamma(y-x)}$ is a steady-state solution of Eq. (21).] Imagine then an observer diffusing through the system with diffusion constant D_T, and which does not interact with the particles. From the point of view of the observer he is static, and the average concentration of particles is constant and equal to γ. Ignoring the half infinite line to his left, the observer could interpret crossings of particles from right to left as "trapping" events, provided that he also interprets crossings from left to right as "birth" events. The apparent rate of birth (crossings from left to right) would be $v_T/a = n[(D + D_T)/a^2 + v/a]$, where $n = \gamma a$ is the average number of particles at the site occupied by the observer. Passing to the continuum limit, we recover the "equivalence" condition, Eq. (42). (Alternatively, one could use the exact discrete result: $\gamma = v/(D + va)$, to obtain the discrete analogue of the equivalence condition: $v_T = v[1 + D_T/(D + va)]$.)

Although shielding breaks down when the trap acts also as a source, one may still look for a solution to the problem in more conventional ways. We were unable to find an analytic solution; however, the discrete equations can be integrated numerically, and the particle system may also be simulated on a computer. Computer simulations confirm the fact that shielding breaks down when $v_T > 0$, and that the particle concentration beyond the nearest particle to the trap is no longer as in equilibrium. In Fig. 3 we show typical results for for various values of v_T. As v_T increases, the concentration of particles near the trap increases, from zero (for $v_T = 0$), to γ (for the appropriate "special" rate, Eq. 42), and to concentrations larger than γ.
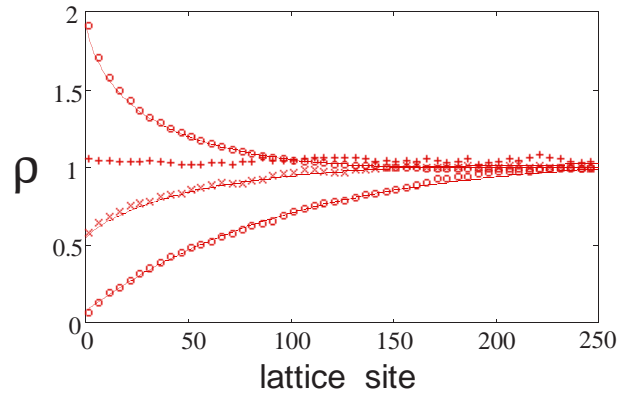

Figure 3. Concentration profile with a trap-source: Shown are results from numerical simulations (symbols) on a lattice of 25,000 sites, averaged over $a^2/D = 10^6$ time steps; as well as results obtained from numerical integration of the exact discrete equations (solid curves). The cases shown are for $v_T/v = 2$, 1, 0.5, and 0 (top to bottom), with $D_T = 0$.

V. DISCUSSION

We have studied diffusion-limited coalescence, $A + A \rightleftharpoons A$, in the presence of a *diffusing* trap, and we have found an exact description of the long-time asymptotic limit, using the IPDF method. When the trap is perfect, the system displays a "shielding" property: the particle nearest to the trap effectively shields the other particles from the trap. That is, the particles remain distributed as in the equilibrium steady-state of the infinite homogeneous system (without a trap), and only the distance between the trap and the nearest particle is unusual. This distance grows linearly with D_T—the diffusion coefficient of the trap.

For an imperfect trap which also acts as a source the shielding property breaks down and we were unable to find an analytic solution, but the *exact* equations can then be solved numerically. We have found an intriguing "equivalence principle": all systems with $v_T = v(1 + D_T/D)$ are equivalent to each other. The trap then seems invisible and the particles remain distributed as in the homogeneous equilibrium state.

Our system is a generalization of von Smoluchowski's model for reaction rates; the particles react with each other, and the trap is mobile. The reaction rate equals the rate of influx of particles into the trap. This rate is $k = n[(D + D_T)/a^2 + v/a]$, where n is the average number of particles at the site adjacent to the trap. For a perfect trap,

we use the result of Eq. (33) to find $n = a^2(d\rho/dx)_{x=0} = a^2\gamma\gamma' = a^2v^2/D(D + D_T)$, and so, in the continuum limit $(a \to 0)$ we get $k = v^2/D$. Curiously, the trapping rate is independent of the diffusivity of the trap, D_T. A faster trap visits more sites per unit time, but it also depletes its immediate neighborhood more effectively, and the two effects cancel each other. For the case of a trap-source, we have failed to obtain an analytic expression for n, and hence we could compute k only numerically.

There remain several interesting open problems. We have considered only the steady state of our model, but the transient is also of interest. For perfect traps the shielding property holds at all times (provided that the initial condition is compatible with it) and one can exploit it to find an analytic answer. An important open problem is that of finding a systematic method for solving the evolution equation for empty intervals. We were fortunate to come across a solution which obeys shielding, but shielding does not always hold, as for example for non-ideal trap-sources. Indeed, most remaining open questions concern the model with a trap-source. An exact analytic solution for this case is still missing. We have managed to prove, however, that the solution could not be of the form of a sum of exponentials (finite *or* infinite), other than for the special states, equivalent to equilibrium.

An interesting question is whether there exist other classes of equivalence. That is, are there any states equivalent to each other, but not to the equilibrium state? —We have managed to prove that such states do not exist, at the level of the empty interval probability. However, there remains the possibility that different systems might share the same *concentration* profile, in spite of differences in their empty interval probabilities. Whether such states exist remains an open challenge.

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